Fluorescence study on the phase transition of hydrogen-bonding gels

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A technique based on steady-state fluorescence measurements is introduced to study the discontinuous volume phase transition of hydrogen-bonding gel. The fluorescence light intensity of pyranine (1-Hydroxypyrene-3, 6, 8-trisulfonic acid) bonded to the gel by means of methacryl amino-propyl-trimethyl ammonium chloride was monitored during the swelling of poly(methacrylic acid-co-dimethyl acrylamide) copolymer in water as a function of temperature. A discontinuous volume phase transition around 60 °C and an additional phase around 30 °C, which may be interpreted as the freely fluctuating phase in a collapsed state, were observed when the fluorescence intensity changes.

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Polymer gels are known to exist in two main phases, swollen and collapsed phases [1,2]. The phase transition, which occurs either continuously or discontinuously, can be induced by changing temperature [3,4], solvent composition [5–7], *p*H of solution, [5,8] ionization degree of network [2,9], or by applying a small electric field [10] or light radiation [11]. The mechanism of the transition can be interpreted as a result of the competition of different fundamental molecular interactions between polymers, which are the ionic, hydrophobic, van der Walls, and hydrogen bonding interactions [1,12]. Recent theoretical and computational studies predict that the collapse phase for heteropolymers should be further classified into three phases: freely fluctuating, e.g., liquid, frozen in degenerate conformations, and frozen in unique conformations (which is known for proteins) [13].

Several experimental techniques have been employed to study the kinetics of swelling or some other aspects of the gels. These include quasielastic light scattering [14], neutron scattering [15], macroscopic experiments [16], *in situ* interferometric measurements [17], and fluorescence measurements [18–20]. However, for collapsed state phases of heteropolymers we have not yet reached the same experimental state of the art. In studies of a gel phase transition, it is some time essential to monitor the change in the microscopic structure of the system, especially around the critical points. In such cases, techniques like small-angle neutron scattering and fluorescence measurements should play crucial a role.

The fluorescence technique is based on the interpretation of the change in emission and/or absorption spectra, emission intensity, and viewing the lifetimes of injected aromatic molecules to monitor the change in their microenvironment. Therefore, it was a natural motivation to study polymer gels using the fluorescence technique so as to elucidate the behavior of the gel by means of change in the microscopic structure as a function of the hydrogen-bonding interactions. This is the main objective of this paper.

At present, we are concerned with phase transitions of poly(methacrylic acid-co-dimethyl acrylamide) co-polymerized with small amount of MAPTAC (methacryl amino-propyl-trimethyl ammonium chloride) to which pyranine (Py) molecules are bonded. The fluorescence intensity of Py was monitored during the swelling of this gel in water as a function of temperature.

Fluorescence spectra are effected by possible environmental features [21–23] such as the interaction with the solvent and other dissolved compounds, temperature, *p*H, concentration of fluorescent species, polarity of solvent or of the fluorescent molecule, and viscosity of the microenvironment around the fluorescent molecule. The environmental effects can cause shifts in fluorescence spectra or change in emission intensity or both of them.

If the concentration of the aromatic molecule is kept small enough, and the possibility of perturbation due to oxygen is excluded the efficiency of emission (or quantum yield) is given by the following relation [21–23]:

$$\frac{I}{I_{\mathrm{abs}}} = \frac{k_r}{k_{\mathrm{nr}} + k_r}, \tag{1}$$

where I is the fluorescence intensity and I_{abs} is the intensity of absorbed light, k_r is the rate constant for radiative transition from the lowest excited state to the ground state (fluorescence), and k_{nr} is the summation of rate constants for internal radiationless (internal conversion) and collisional quenching processes. If I_{abs} is kept fixed during the experiments (*steady-state* fluorescence experiments), radiative and nonradiative rate constants determine the fluorescence intensity.

In this study, these properties of Py were employed to monitor the swelling of the hydrogen-bonding gel.

The gel was prepared by standard radical polymerization: 6*M* methacrylic acid (polymer constituent), 2*M* dimethylacrylamide (polymer constituent), 100m*M* bisacrylamide (cross linker), 9.74m*M* of 2, 2′ azobis (isobutyronitrile) (initiator), and 1.2m*M* MAPTAC (cationic constituent) were dissolved in dimethyl sulfoxide (DMSO). 0.4m*M* Py was added to the pregel solution. Pyranine can be trapped randomly in the gel by means of MAPTAC molecules (see Fig. 1).

The pregel solution was degassed, and the gelation was carried out at 60 °C for 24 h in glass tubes having an inner diameter of 8.5 mm. After gelation was completed, the gels were crushed into small pieces and immersed in a large vol-

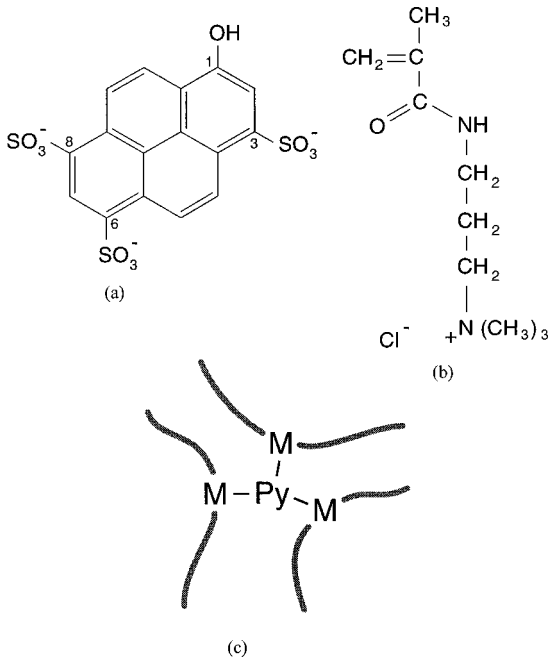


FIG. 1. Pyranine (a) and MAPTAC monomer (b). Py has three sites that can bond to MAPTAC (c).

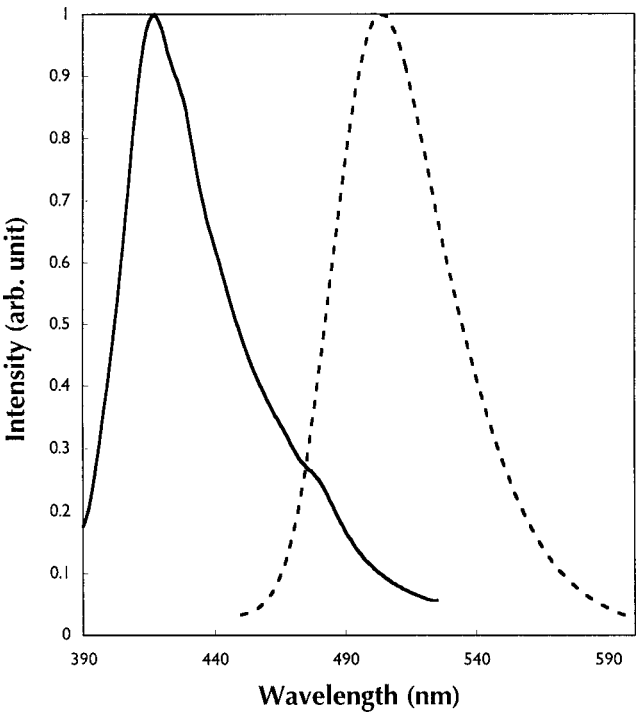


FIG. 2. Normalized emission spectra of the pyranine from the washed gel (——) and from the Py-water solution (---). There is no shift of the emission peaks in either the washed gel or the Py-water solution at various temperatures between 20 and 90 °C.

ume of basic solution (pH 11 NaOH). Once the gels reached the swelling equilibrium, they were washed with pure water for several days to remove any unreacted residuals and DMSO. These gels were then placed in an acidic solution (pH 3 HCl) to bring the gels back to the collapsed state after which they were washed again many times with pure water. For our fluorescence experiments, these washed gels were put in long glass tubes, which were sealed in order to prevent diffusion of oxygen into the gel during the swelling.

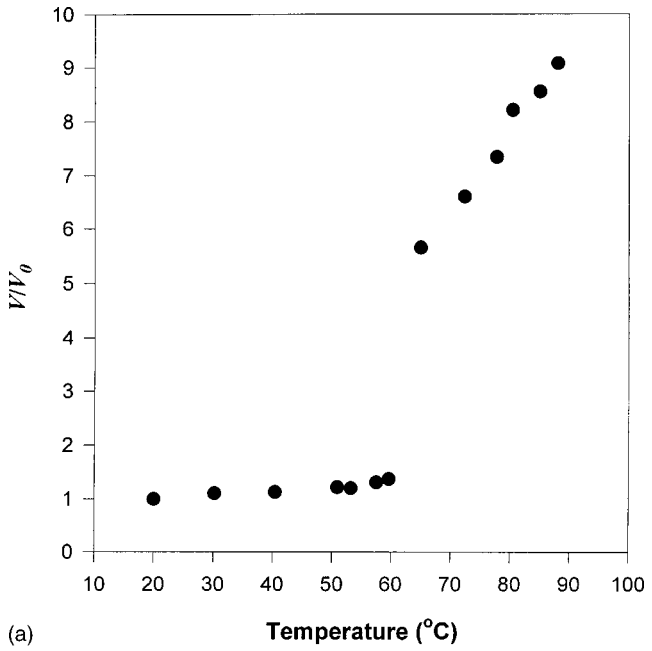
We compared the emission spectrum of Py trapped in the gel with that of the 0.4mM Py-water solution (same concentration as the pregel solution).

Fluorescence measurements were carried out using a SPEX model DM3000-F spectrofluorimeter equipped with a temperature controller. All measurements were made at the 90° position and slit widths were kept at 2 mm. During the washing process two distinct emission spectra were observed from the gel; the one has the maxima at 419 nm wavelength (corresponding to Py's bonded to the gel) and the other one that has the maxima at 504 nm wavelength (corresponding to the free Py's in the gel). When the washing process was complete, the 504 nm peak disappeared entirely, showing that no free Py's were left in the gel.

After the washed gels reached equilibrium, both the gel and the Py-water solution were illuminated, in turn, by 374 nm light and their emission spectra were recorded at various temperatures between 20–90 °C. At the same time, the final volume of the gel at each temperature was measured by recording the level of these crushed gel particles. In Fig. 2 the normalized emission spectra of Py from both the washed gel and the Py-water solution are shown. The maxima of emitted light of the gel and the Py-water solution are clearly different from each other. The wavelength of the light corresponding to the maxima of emission peaks were 419 and 504 nm for the washed gel and Py-water solution, respectively.

No shifts were observed at the wavelengths corresponding to the emission maxima from either the washed gel or Py-water solution, and no appreciable change was seen in the intensity of Py-water solution as the temperature was varied. No peak in the emission spectra of Py from the gel was observed at 504 nm, indicating that some of the Py's were released into the water during the swelling of the gel.

Two factors affect the emission intensity: One is directly related to the Py concentration in the gel. Since the Py's are attached to the gel by coulombic attractions with MAPTAC, as the gel swells, the concentration of Py in the gel and, therefore, also that in the region illuminated by excitation light will decrease. This decrease in Py concentration will cause a decrease in the emission intensity I. The other effect is related to the structural change in the gel. In the collapsed state, Py molecules are trapped in very small spaces because of the compactness of the gel. As the swelling proceeds, the viscosity of the gel changes leading to the change in microenvironment around Py molecules. The ability of Py to move freely in the enlarged space and the probability of Py colliding with water molecules increase when the volume of the gel is increased. The role of the solvent in such a picture is to add the quasicontinuum of states needed to satisfy energy resonance condition. The solvent (water) acts as an energy sink for rapid vibrational relaxation that occurs after the rate-limiting transition from the initial state. As discussed earlier, this effect will cause a decrease in intensity by causing an increase in the nonradiative probability k_{nr}.



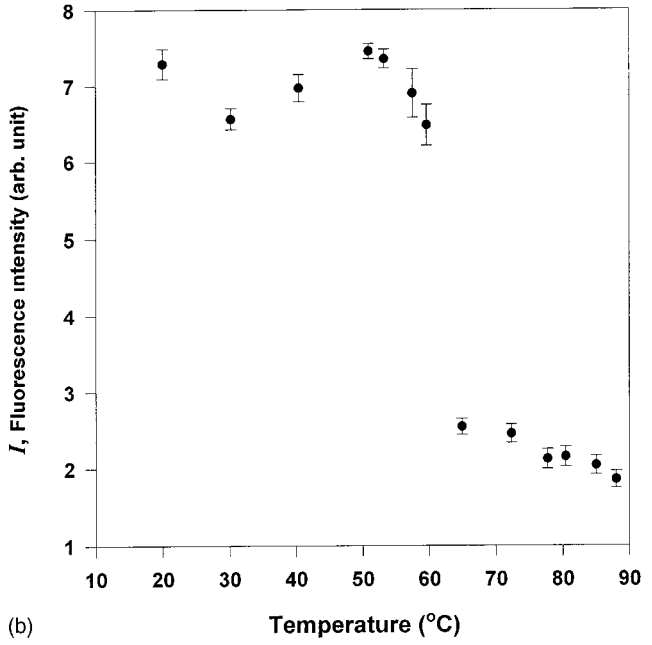


FIG. 3. Dependence of the swelling V/V_0 (a) and the normalized intensity of the emission, I (b) on temperature.

To get rid of the first effect (change in Py concentration) so that we can see solely the intensity change that depends on the change in microenvironment around the Py molecules, we corrected the measured intensity I_m as follows:

$$I=(V/V_0)I_m, \tag{2}$$

where V and V_0 are the volumes at the temperatures in question and at 20 °C (initial volume), respectively. The factor V/V_0 keeps the concentration fixed for all stages.

The volume ratio V/V_0 and normalized emission intensity I of Py from the gel versus temperature are shown in Fig. 3. Although there was no appreciable change in the volume, a considerable decrease in the fluorescence intensity was observed around 30 °C in the collapsed state. A sudden decrease was observed in the intensity (at 419 nm) about 60 °C corresponding to the sudden increase in the volume of the gel and then a gradual change from 60–90 °C.

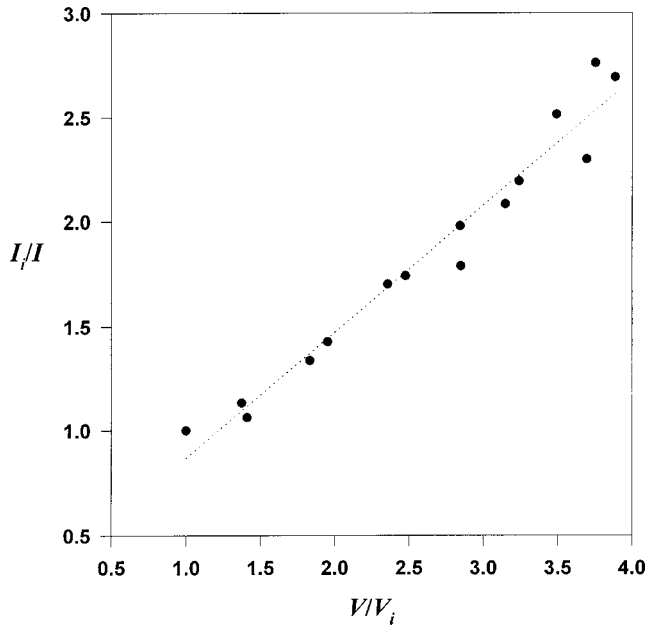


FIG. 4. Dependence of the fluorescence intensity ratio I_i/I on the volume ratio V/V_i in the region of discontinuous volume phase transition.

We also observed that the intensity ratio I_i/I, in the region at which the discontinuous volume transition takes place, is linearly proportional to the volume ratio V/V_i as plotted in Fig. 4, where V_i and I_i are the initial volume and intensity at the beginning of the sudden change in the *volume-temperature* and *intensity-temperature* plots, respectively. V and I are the volume and intensity measured in time during the discontinuous volume change at the transition temperature.

As a result, methacrylic acid and dimethyl acrylamide form polycomplexes in solution via hydrogen bonding. The electrostatic attraction between MAPTAC and Py molecules causes trapping of Py molecules inside the gel. Below certain temperature, the gel is in the collapsed state due to the hydrogen bonding between the polymer segments comprising the gel. When a critical temperature is reached the hydrogen bonds between these segments are broken, allowing entropy to increase and induce a discontinuous volume change in the gel.

Figure 4 shows an inverse linear relation between V and I. This means that a change in the volume causes some change in the emission intensity, which is an expected behavior for a fluorescence probe, i.e., as the gel swells the intensity of the probe molecules decreases. However, an unexpected behavior in the intensity-temperature curve was observed in the collapsed state. Although no appreciable change was observed in the volume, a considerable decrease in the fluorescence intensity (about 16% of the maximum intensity) was observed around 30 °C. This decrease in intensity may be attributed to the probe molecules being relatively free around

30 °C. Since Py's are bonded to the gel over the MAPTAC molecules, the gel should be fluctuating freely as a liquid. Thus, the behavior of the intensity data around 30 °C might be interpreted as an indication of the phase transition from probably frozen-in degenerate conformations to freely fluctuating phase in the collapsed state. It may not be possible at this stage to distinguish these distinct phases, but it seems that the phase at 30 °C is, comparatively, a more freely fluctuating phase.

The weak dependence of the intensity on volume change above 60 °C may be explained by two possible assumptions.

(i) The quenching of Py reaches saturation when the solvent uptake reaches a certain value. More solvent, above this certain value, cannot effect the nonradiative transition probabilities of Py.

(ii) Py's are bonded to the strands of the gel via three ends. Each of the strands may be treated as a spring. Up to some degree of the solvent uptake, Py will move freely since the ''springs'' are not stretched and have the chance to move in relatively big volume. Above a certain degree of solvent uptake the ''springs'' will start to get tightened, thus the free volume for Py will be smaller and smaller as the swelling progresses, and this will cause a weak dependence of the intensity on the volume change towards the final stage of swelling. These two estimations may also be effective on the intensity together.

The linear relation between $1/I$ and V, at the critical temperature, at which discontinuous volume phase transition takes place from the collapsed phase to the swollen phase, may allow one to perform *in situ* fluorescence experiments on the volume phase transition of the aromatic molecule bonded gels.

In addition to providing the fluorescence technique to study the phase transitions of the hydrogen-bonding gels, this work also shows the feasibility of using this technique to understand some other important aspects of the gels. For example, when aromatic molecules chosen as a target diffuse into the gel they may be bonded to the gel by means of absorption sites or move freely in the gel; or some of the target molecules are bonded to the gel while the others may move freely in the gel. The bonded or unbonded target molecules can be distinguished by means of their distinct emission spectra, and a quantitative analysis of the bonded or unbonded molecules can be possible by this method for the gels in different states, swollen or collapsed. Thus the recognition of a target molecule by gels, which is very important technically and for the study of imprinting gels and biological systems, may be studied by this method.

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